A NEW APPROXIMATION FOR THE EQUATION OF STATE, VALID FOR LIQUID AND GAS

THESIS

SUBMITTED BY

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A NEW APPROXIMATION FOR THE EQUATION OF STATE, VALID FOR LIQUID AND GAS.

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Introduction

It has been only recently that a satisfactorily general kinetic theory of liquids[1),(2),(3),(4)], capable of describing the equilibrium as well as the dynamical properties of a statistical assembly of molecules has been developed. In the second of this series of papers by Professor Max Born and Dr. H.S.Green[(2)], the latter devoted some attention to the problem of condensation, and a new equation of state was obtained, valid for both phases, liquid and gas.

The present work is particularly concerned with the study of that equation of state, with a view to adapting it for numerical evaluation. In the course of our investigation it has been found that some thermodynamical expressions, including that of the equation of state, as given in the original paper[(2)], are not correct. A new equation, which keeps the main features of the old one has now been obtained and is given in Chapter III.

The final expressions, giving the internal and the free energy, and the equation of state itself, involved the solution of some integro-differential equations, in order to solve which several assumptions were made. We have considered it important to include two chapters

discussing the extent to which these assumptions may influence the final range of validity of the thermodynamical expressions. Most of these results are contained in the paper by Green, mentioned above.

The equation of state, which has been obtained, is of course approximate; but it covers both phases, liquid and gas, this being the main feature of the theory. The liquid differs from the gas by the existence of real roots of a certain transcendental equation. This equation, which in the original form contains an integral in the left hand-side, has now been reduced, by using a suitable expansion, to an algebraic rapidly convergent series. In this form it is easy to make its analytic continuation without falling into ambiguities of any kind. The expansion also provides the way of finding its complex and real roots.

The theory of condensation developed by Mayer[5] and others[6],[7],[8], is confirmed by the present theory to the extent that a divergence of the cluster series is found, which is intimately associated with the process of condensation. On the exact point at which this divergence occurs detailed calculations do not confirm that it happens at the density of the saturated vapour. The isotherm is continued into the metastable region above this density, arising to a maximun and falling to a subsequent minimun as the density is increased, much in the way foreshadowed by Van der

Waals over fifty years ago. The point of divergence is found as separating the metastable states of the liquid from those of the gas. This point, which from our standpoint may be considered as a sort of branch point is identified with that point at which one of the complex roots of the transcendental equation becomes real. In this way the thermo-dynamical properties are regulated through the nature of the roots of this equation.

The main object of the present paper is connected with the solution of this transcendental equation. The author has succeeded, as has been said, in reducing the problem to the solution of an algebraic equation of $2n+1^{th}$ degree, $2n+1$ being the number of terms used in the approximation. One of the chapters is entirely devoted to a detailed exposition of the method in the most general form.

In chapter VI, the equation of state is given in terms of the expansion, to show how the method permits the actual evaluation of some integrals involving the complex roots of the transcendental equation.

Finally a numerical computation has been carried out for Argon; two isotherms have been calculated, one for the critical temperature, the other for a much lower one. A chapter includes the complete calculations for one of the isotherms, that for the critical temperature, in order to show clearly the advantages of the method. It also provides the means for controlling

the results.

In this numerical computation, a rather drastic approximation has been used. In point of fact, only the first three roots of the equation have been taken into account. The previous assumptions, which are discussed in the first and second chapters, already introduce some approximations, which seem to the author to be of the same order of magnitude as that involved in the present evaluation. Better results could perhaps be obtained by taking into account as many as five roots. But in spite of this crude numerical computation, it is clearly shown that the approximation is able to penetrate beyond the singularity into the liquid region.

In chapter IV we refer incidentally to the free energy. Here also, it has been found that the expression as given in the original paper by Green[2] is incorrect. This difficulty, however, has been overcome; but the present expression is valid only approximately. The reason which prevented us in obtaining the exact solution is related to the appearance of a certain parameter which was assumed to be a constant, but in fact, is a function of temperature and density. For the perfect gas, i.e. over the Boyle point, at which temperature the first virial coefficient vanishes, this parameter becomes identical with unity; but for lower temperatures its value may deviate quite largely from it. We have been able to give an explicit expression for this pa-

rameter,as a function of temperature and density. It is a very significant fact that it is by the introduction of this dependence on temperature and density of the parameter,that the critical volume as obtained from our calculations is nearly equal to that given by experiment. If on the contrary the value of the parameter is assumed to be constant and equal to unity for all values of temperature and density ,the critical volume turns out to be twice as large as the actual experimental value.

Further it can be inferred from experiment that the branch point should move with decreasing temperature to higher densities; this would not result from the theory if the parameter is taken as a constant, but is obtained correctly if it is determined as a function of temperature as described.

The author would here gratefully acknowledge the debt he owes to Professor Max Born,who suggested the subject of this work,supervised its execution and gave the author invaluable advice and encouragement. He also is indebted to Dr. H.S.Green for many helpful suggestions.

CHAPTER I. THE KIRKWOOD OR SUPERPOSITION APPROXIMATION.

As we have indicated in the Introduction we start by recapitulating very briefly those parts of Professor Born's and Dr. H.Green's papers which have a direct bearing upon our work. It will make it possible to discuss the range of validity of some approximations which are introduced in order to solve some complicated integro-differential equations.

We consider an assembly of N molecules confined within the volume V. The position of the ith. molecule will be specified by the vector $\underline{x}^{(i)}$, its velocity by $\underline{\xi}^{(i)}$, its acceleration by $\underline{\eta}^{(i)}$, etc.

We denote by $n_h(t, \underline{x}^{(1)}, \underline{x}^{(2)}, \ldots \underline{x}^{(h)}) \prod_{i=1}^{h} d\underline{x}^{(i)}$, the probability that h distinct molecules occupy volume elements $d\underline{x}^{(1)}, d\underline{x}^{(2)}, \ldots\ldots d\underline{x}^{(h)}$ located at $\underline{x}^{(1)}, \underline{x}^{(2)}, \ldots\ldots \underline{x}^{(h)}$ respectively at time t. According to this notation n_1 is the number density, and n_2/n_1^2 the radial distribution function of the molecular assembly in isotropic conditions. In a similar way we denote by $f_h(t, \underline{x}^{(1)}, \ldots\ldots \underline{x}^{(h)}, \underline{\xi}^{(1)}, \ldots\ldots \underline{\xi}^{(h)}) \prod_{i=1}^{h} d\underline{x}^{(i)}\, d\underline{\xi}^{(i)}$, the probability that h molecules, with their velocities in the range $\underline{\xi}^{(i)}$, $d\underline{\xi}^{(i)}$, occupy the volume elements $\underline{x}^{(i)}$, $d\underline{x}^{(i)}$ at time t. Here f_1 is the velocity distribution function employed in the kinetic theory of gases. It follows from its definition that f_h satisfies the equation

$$(1.1) \quad \int^{(h)} \cdots \int f_h(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h)}, \underline{\xi}^{(1)}, \ldots \underline{\xi}^{(h)}) \prod_{i=1}^{h} d\underline{\xi}^{(i)} = n_h(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h)})$$

Similarly $g_h(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h)}, \underline{\xi}^{(1)}, \ldots \underline{\xi}^{(h)}, \underline{\eta}_1, \ldots \underline{\eta}^{(h)})$ is defined by

$$(1.2)\quad \int^{(h)}\cdots\int g_h(t, \underline{x}, \underline{\xi}, \underline{\eta}) \prod_{i=1}^{h} d\underline{\eta}^{(i)} = f_h(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h)}, \underline{\xi}^{(1)} \ldots \underline{\xi}^{(h)})$$

For distribution functions of the same kind we have, with a suitable normalisation factor:

$$(1.3)\quad \int \eta_{h+1}(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h+1)})\, d\underline{x}^{(h+1)} = (N-h)\, n_h(t, \underline{x}^{(1)}, \ldots \underline{x}^{(h)})$$

and

$$(1.4)\quad \int f_{h+1}(t, \underline{x}^{(1)}, \ldots \underline{x}^{h+1}, \underline{\xi}^{(1)} \ldots \underline{\xi}^{(h+1)})\, d\underline{x}^{h+1}\, d\underline{\xi}^{h+1} = (N-h)\, f_h(t, \underline{x}, \underline{\xi})$$

and also for higher distribution functions.

From these definitions there follows, by simple consideration, the equation of continuity which reads

$$(1.5)\quad \frac{\partial n_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial}{\partial \underline{x}^{(i)}} (n_h \cdot \overline{\underline{\xi}}^{(i)}) = 0$$

where

$$(1.6)\quad \overline{\underline{\xi}}^{(i)} = \frac{1}{n_h} \int^{(h)}\cdots\int f_h\, \underline{\xi}^{(i)} \prod_{i=1}^{h} d\underline{\xi}^{(i)}$$

is the average velocity of the ith. molecule in a group of h molecules whose positions are specified. It follows, by a similar reasoning that f_h satisfies the equation

$$(1.7)\quad \frac{\partial f_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial f_h}{\partial \underline{x}^{(i)}} \underline{\xi}^{(i)} + \sum_{i=1}^{h} \frac{\partial}{\partial \underline{\xi}^{(i)}} (f_h \overline{\underline{\eta}}^{(i)}) = 0,$$

where

$$(1.8)\quad \overline{\underline{\eta}}^{(i)} = \frac{1}{f_h} \int^{(h)}\cdots\int g_h\, \underline{\eta}^{(i)} \prod_{i=1}^{h} d\underline{\eta}^{(i)}$$

is the average acceleration of the ith. molecule in a group of h molecules with specified positions and velocities.

We now assume that the potential function Φ can be expressed in the form

$$\Phi = \frac{1}{2} \sum_{i,j=1}^{N} \phi^{(ij)} \tag{1.9}$$

where $\phi^{(ij)} = \phi(\underline{x}^{(i)}, \underline{x}^{j})$ is the mutual potential energy of two molecules at $\underline{x}^{(i)}$ and $\underline{x}^{(j)}$. In what follows it will be assumed that the intermolecular forces are central forces, i.e. $\phi^{(ij)}$ will depend only on the distance $|\underline{x}^{(i)} - \underline{x}^{(j)}|$ between the two molecules.

Since the acceleration of a molecule at a point $\underline{x}^{(i)}$ is given by

$$\underline{\eta}^{(i)} = -\frac{1}{m} \sum_{j=1}^{N} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} \tag{1.10}$$

it follows an alternative expression to (1.8) for the mean acceleration

$$\overline{\underline{\eta}^{(i)}} = -\frac{1}{m} \sum_{j=1}^{h} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} - \frac{1}{m f_h} \iint \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}} d\underline{x}^{(h+1)} d\underline{\xi}^{(h+1)} \tag{1.11}$$

If we insert this expression in (1.7) we obtain the fundamental equation

$$\frac{\partial f_h}{\partial t} + \sum_{i=1}^{h} \frac{\partial f_h}{\partial \underline{x}^{(i)}} \underline{\xi}^{(i)} = \frac{1}{m} \sum_{i,j=1}^{h} \frac{\partial f_h}{\partial \underline{\xi}^{(i)}} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} + \tag{1.12}$$

$$+ \frac{1}{m} \iint \sum_{i=1}^{h} \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}} \frac{\partial f_{h+1}}{\partial \underline{\xi}^{(i)}} d\underline{x}^{(h+1)} d\underline{\xi}^{(h+1)}$$

We are particularly interested in the solution of

equation (1.12) for the case of equilibrium, where

$$\frac{\partial f_h}{\partial t} = 0 \tag{1.13}$$

The solution is of the form

$$f_h = n_h \left(\frac{m}{2\pi kT}\right)^{3h/2} e^{-\frac{m}{2kT}\sum_{i=1}^{h} \xi^{(i)2}} \tag{1.14}$$

provided n_h satisfies the equation

$$\frac{\partial n_h}{\partial \underline{x}^{(i)}} + \sum_{j=1}^{h} \frac{n_h}{kT} \frac{\partial \phi^{(ij)}}{\partial \underline{x}^{(i)}} + \int \frac{n_{h+1}}{kT} \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}^{(i)}} d\underline{x}^{(h+1)} = 0 \tag{1.15}$$

Equation (1.15) constitutes now the fundamental equation. Its solution may be obtained following two different procedures. The first one consists of putting first h=N and observing that $n_{h+1}=0$. This gives

$$Q n_N = e^{-\Phi/kT} \tag{1.16}$$

where

$$Q = \frac{1}{N!} \int^{(N)} \cdots \int e^{-\Phi/kT} \prod_{i=1}^{N} d\underline{x}^{(i)} \tag{1.17}$$

(1.17) is obtained easily by repeated use of (1.3). One obtains then as the formal solution of (1.15),

$$n_h = \frac{N!}{(N-h)!} \frac{\int^{(N-h)} \cdots \int e^{-\Phi/kT} \prod_{i=h+1}^{N} d\underline{x}^{(h+1)}}{\int^{(N)} \cdots \int e^{-\Phi/kT} \prod_{i=1}^{N} d\underline{x}^{(i)}} \tag{1.18}$$

It is obvious that even for the simplest type of potential function the integrals that appear in (1.18) are exceedingly complicated.

In practice a second procedure is preferable, since usually one is only interested in obtaining solutions for h small. In particular we are interested in the case h=2, i.e. in finding the form of the radial distribution function.

But using this procedure one is faced inevitably with an assumption regarding the form of n_3 which appears under the integrand of (1.15) when putting h=2.

The form adopted for n_3 is expressed by

$$(1.19)\quad n_3(\underline{x}^{(1)}, \underline{x}^{(2)}, \underline{x}^{(3)}) = \frac{n_2(\underline{x}^{(3)}, \underline{x}^{(2)})\, n_2(\underline{x}^{(3)}, \underline{x}^{(1)})\, n_2(\underline{x}^{(1)}, \underline{x}^{(2)})}{n_1(\underline{x}^{(1)})\, n_1(\underline{x}^{(2)})\, n_1(\underline{x}^{(3)})}.$$

which expresses, that the relative probability $n_3 / n_1^3 n_2^{(1.2)}$ of the occurrence of a molecule $\underline{x}^{(3)}$ in conjunction with two others should be the product of the relative probabilities $n_2^{(3.1)} / n_1^{(3)} \cdot n_1^{(1)}$ and $n_2^{(3.2)} / n_1^{(3)} \cdot n_1^{(2)}$ of the occurrence of the same molecule in conjunction with each of the others separately.

(1.19) holds only approximately sice in the case of liquids the molecules are not independent. It is known as the 'superposition approximation'. We have some reasons to presume that one can rely on its validity even for high densities and low temperatures. The first one is based on the results which were obtained by Kirkwood who was the first to suggest and apply it.

The second reason is based on the fact that (1.19) holds exactly for solids, as has been shown by a member of the Department of Mathematical Physics, Edinburgh University, A.A. Sabry (not published).

If one introduces (1.19) in (1.15) after putting h/2 one obtains:

$$(1.20)\qquad \frac{\partial n_2(\underline{x}^{(1)}, \underline{x}^{(2)})}{\partial \underline{x}^{(2)}} + \frac{n_2(\underline{x}^{(1)}, \underline{x}^{(2)})}{kT} \frac{\partial \phi^{(1,2)}}{\partial \underline{x}^{(2)}} =$$

$$= \frac{n_2(\underline{x}^{(1)}, \underline{x}^{(2)})}{kT} \int n_2(\underline{x}^{(2)}, \underline{x}^{(3)})\, n_2(\underline{x}^{(3)}, \underline{x}^{(1)}) \frac{\partial \phi^{(2,3)}}{\partial \underline{x}^{(3)}} d\underline{x}^{(3)}$$

(1.20) can be finally brought to the form (see appendix II in paper quoted as (2)),

$$(1.21)\qquad \log \frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT} =$$

$$= \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^{s} (s^2 - t^2) \frac{t+r}{r} \{ n_2(t+r) - n_1^2 \}\, dt\, n_2(s) \frac{\phi'(s)}{kT}\, ds$$

the two functions $n_2(r)$ and $\phi(r)$ depend only on the distance r between the two molecules. Equation (1.21) was obtained first by Kirkwood in 1933 for a general potential and used by Kirkwood and Boggs [9] in 1942 for 'rigid spherical molecules'. It has been shown to give solutions which are in accordance with experimental data provided by the study of X-Ray scattering by monoatomic liquids.

CHAPTER II. THE SOLUTION OF THE INTEGRAL EQUATION.

The solution of equation (1.21) requires still a new approximation. We write it here again

$$\log \frac{n_2(r)}{n_1^2} + \frac{\phi(r)}{kT} = \frac{\pi}{n_1^3} \int_0^\infty \int_{-s}^{s} (s^2 - t^2) \frac{t+r}{r} \{ n_2(t+r) - n_1^2 \} dt \, n_2(s) \frac{\phi'(s)}{kT} ds \tag{2.1}$$

A look to (2.1) shows immediately that the integrand contains $n_2(r)$ quadratically. In order to linearize the equation it is assumed that $n_2(r)$ is of the form

$$n_2(r) = n_1^2 \, e^{-\phi(r)/kT} + f(r) \tag{2.2}$$

Inserting (2.2) in (2.1) one obtains

$$r \cdot f(r) = -\pi n_1 \int_0^\infty \int_{-s}^{s} (s^2 - t^2)(t+r) f(t+r) \{ 1 + \alpha(t+r) \} dt \, \alpha'(s) \{ 1 + f(s) \} ds$$
$$- \pi n_1 \int_0^\infty \int_{-s}^{s} (s^2 - t^2)(t+r) \alpha(t+r) dt \, \alpha'(s) \{ 1 + f(s) \} ds \tag{2.3}$$

where

$$\alpha(r) = e^{-\phi(r)/kT} - 1$$

Let us discuss briefly the way in which (2.3) is obtained: while the left hand-side follows rigurously, the right hand-side is only approximate since cubes and higher powers of $f(r)$ have been neglected. This seems to us to be very reasonable. In fact, it may be inferred from experimental data that even for rather low temperatures and high densities the maximun absolute value of $f(r)$ is of the order of 0.4, which implies neglecting terms that amount to a 1% of the total value.

We shall see later on, that the final expression for $n_2(r)$ obtained using this approximation is substantially equivalent to that obtained by Montroll and Mayer [10] in 1941.

Following Green, we observe now, that $\alpha(r)$ and $\alpha'(r)$ are both negligible except for small r, so that, when multiplied by these factors, $f(r)$ may be replaced by $(\epsilon - 1)$, its average value in the neighbourhood of the origin. It has been shown by Green [2] that $\epsilon = 1$ when we are in the gas region i.e. for low densities and high temperatures. But it is also clear that ϵ is actually a function of these two variables. We have paid some attention to this problem and found an explicit expression for ϵ in terms of both variables, which shows that its value may deviate quite largely from unity for low temperatures. On the other hand it may be considered practically constant with respect to density. This will make it possible to find an explicit expression for the free energy.

After integration by parts, (2.3) becomes

$$(2.4)\quad r \cdot f(r) = 2\pi n_1 \int_0^\infty \int_{-s}^{s} (t+r)\{f(t+r) + \epsilon\,\alpha(t+r)\,dt\,\epsilon\,\alpha(s).s\,ds$$

Equation (2.4) is solved by Fourier transform. If one writes

$$(2.5)\qquad r \cdot g(r) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} s \cdot f(s) \sin(rs)\,ds$$

and

(2.6) $$r.\,\beta(r) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} s.\,\alpha(s)\,\sin(rs)\,ds$$

then (2.4) becomes

(2.7) $$\lambda\, g(r) = \{\, g(r) + \epsilon\beta(r) \,\}\, \epsilon\beta(r)$$

where

(2.8) $$\lambda = \frac{1}{(2\pi)^{3/2} n_1}$$

We obtain finally

(2.9) $$r.f(r) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{\epsilon^2.\, s.\, \beta^2(s)\, \sin(rs)\, ds}{\lambda - \epsilon\beta(s)}$$

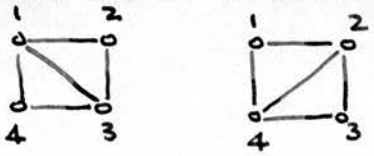
At this point we wish to compare our results with those of Montroll and Mayer [10]. They have found for the radial distribution function, which we denote by $n_2^{(M)}(r)$, the following expression:

(2.10) $$n_2^{(M)}(r) = n_1^2\, e^{-\phi(r)/kT} \left\{ 1 + \frac{1}{(2\pi)^{1/2} r} \int_{-\infty}^{\infty} \frac{s.\,\beta^2(s)\,\sin(rs)\,ds}{\lambda - \beta(s)} + \right.$$
$$\left. + (2\pi)^{3/2 - m} \sum_{m=2}^{\infty} \lambda^{-m}\, H_{2,m}^{(1)} + \cdots \right\}$$

where $H_{2,m}^{(1)}$, $H_{2,m}^{(2)}$, etc. represent integrals over chains of molecules with one internal connection, two internal connections, etc. respectively. We have for $m=2$, for instance

(2.11) $$H_{2,2}^{(1)}(\underline{x}^{(3)}, \underline{x}^{(4)}) = \frac{1}{2!} \iint \left(\alpha^{(12)}\alpha^{(23)}\alpha^{(34)}\alpha^{(41)}\alpha^{(13)} + \right.$$
$$\left. + \alpha^{(12)}\alpha^{(23)}\alpha^{(34)}\alpha^{(41)}\alpha^{(24)} \right) d\underline{x}^{(1)} d\underline{x}^{(2)}$$

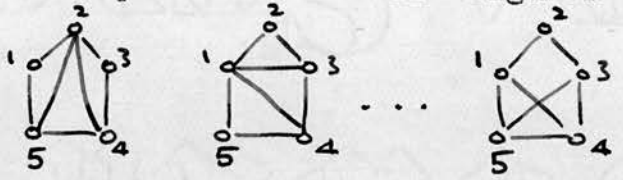
which correspond to the well known 'bond figures'



For $m=3$ we have for instance:

$$(2.12)\quad H^{(2)}_{2,3}(\underline{x}^{(4)},\underline{x}^{(5)}) = \frac{1}{3!}\iiint \Big\{ \alpha^{(12)}\alpha^{(23)}\alpha^{(34)}\alpha^{(45)}\alpha^{(51)}\alpha^{(24)}\alpha^{(25)} + \alpha^{(12)}\alpha^{(23)}\alpha^{(34)}\alpha^{(45)}\alpha^{(51)}\alpha^{(13)}\alpha^{(14)} + \cdots\cdots \Big\} d\underline{x}^{(1)} d\underline{x}^{(2)} d\underline{x}^{(3)}$$

which correspond to the 'bond figures'



etc.

If we now expand (2.2) we get

$$(2.13)\quad n_2(r) = n_1^2 e^{-\phi(r)/kT}\left\{1 + f(r) + \frac{f^2(r)}{2!} + \frac{f^3(r)}{3!} + \cdots\right\}$$

Inserting (2.9) we obtain

$$(2.14)\quad n_2(r) = n_1^2 e^{-\phi(r)/kT}\left\{1 + \frac{1}{(2\pi)^{3/2}\, r}\int_{-\infty}^{\infty} \frac{\epsilon^2 s\, \beta^2(s)\sin(rs)\, ds}{\lambda - \epsilon\beta(s)} + \cdots\right\}$$

Comparing (2.14) with (2.10), we see that for the special case $\epsilon = 1$ both expressions are identical except by terms in higher powers of $f(r)$ which seem to be then equivalent to the terms under the complicated integrals $H^{(1)}_{2,m}$, $H^{(2)}_{2,m}$, etc. The effect of averaging and introducing ϵ may therefore be considered as a further refinement. In fact one could still perform an expansion in powers of $(\epsilon - 1)$ and both expressions could be considered equivalents if one

identifies the remaining terms, coming in one hand from higher powers of $f(r)$ and on the other hand from the expansion, with those terms of (2.10) which appear under the summation in the form of complicated integrals. It is a very significant fact that ϵ, as will be shown in next chapter, only becomes equal to unity for temperatures and densities corresponding to the perfect gas, in which case (2.10) and (2.14) become identical with one another.

It seems to us that Mayer and Montroll have underestimated the range of validity of its equation (2.10), since according to what follows in the paper mentioned above, it was only used as an approximation in the gas phase.

We assume now that there is an analytical function $\beta(z)$ which reduces to $\beta(r)$ for $z = r$ real. (2.9), then is the most general solution of (2.4) if the path of integration is chosen as any course from negative to positive infinity in the complex z-plane, and in particular incloses those points z_μ for which the following transcendental equation

$$\beta(z) = \lambda/\epsilon \tag{2.15}$$

is satisfied.

We shall now define $\beta(z)$ for complex z. For doing it we assume that $s \cdot \alpha(s)$ admits an expansion of the type

$$(2.16) \qquad s.\alpha(s) = \sum_{-\infty}^{\infty} c_k e^{is\xi_k}$$

ξ_k being a complex number in the upper half of the complex plane. This way of expanding the function $s.\alpha(s)$ is based on the fact that for all $s > s_0$ we have practically $s.\alpha(s) = 0$, as shown in figure 1.

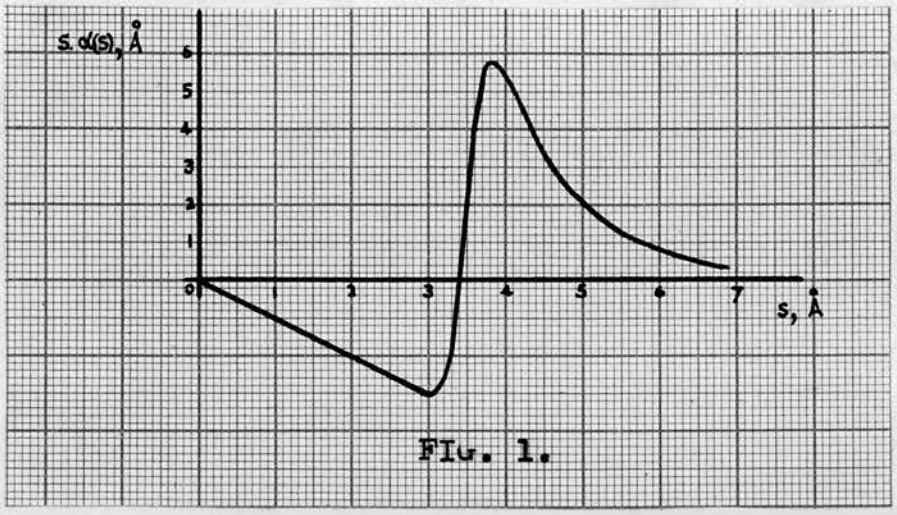


Fig. 1.

By a proper choice of the form of the ξ_k, as will be shown clearly in chapter V, $s.\alpha(s)$ can be assumed to be represented by the expansion (2.16).

From (2.6), which gives the definition of $\beta(r)$ for r real, we get after inserting (2.16),

$$(2.17) \qquad r\,\beta(r) = \frac{2}{(2\pi)^{1/2}} \sum c_k I_k$$

where

$$(2.18) \qquad I_k = \int_0^{\infty} e^{is\xi_k} \sin(rs)\, ds$$

Integration by parts gives, remembering that ξ_k is a complex number in the upper half of the complex plane,

(2.19) $$I_k = \frac{-r}{\xi_k^2 - r^2}$$

which introduced in (2.17) gives

(2.20) $$\beta(r) = -\frac{2}{(2\pi)^{1/2}} \sum_k \frac{c_k}{(\xi_k^2 - r^2)}$$

This equation has been obtained in the assumption that r is real and is therefore valid for the real axes. The function in the right hand-side however is an analytic function of r except for the occurrence of simple poles at the points $\pm \xi_k$. The equation (2.20) may therefore be regarded as a satisfactory definition of the function $\beta(r)$ for all values of r real and complex, satisfying the following conditions:

(a) $\beta(z)$ reduces to $\beta(r)$ for $z = r$ real

(b) $\beta(z) \to 0$ as $|z| \to \infty$, uniformly with respect to arg z, in the upper half of the z-plane.

CHAPTER III. THE EQUATION OF STATE.

The pressure p is given [2] by

$$p = n_1 kT - \frac{1}{6}\int_0^\infty n_2(r)\,\phi'(r)\,4\pi r^3\,dr \tag{3.1}$$

In order to obtain an explicit expression for p, we now expand (2.2) and take only the linear term in $f(r)$, i.e.

$$n_2(r) = n_1^2\, e^{-\phi(r)/kT}\,\{1 + f(r)\} \tag{3.2}$$

This approximation is also reasonable; for $r > r_1$, r_1 being the value of r for which $n_2(r)$ has its absolute maximun, when one substitutes (3.2) in the integral appearing in (3.1), squares and higher powers of $f(r)$ will not give an appreciable contribution, since the effect of the total correction $e^{f(r)}$ is to superimpose on the first factor $n_1^2 . e^{-\phi(r)/kT}$ oscillations around a constant value which will cancel one another when performing the integration. Contributions coming from squares and higher powers of $f(r)$ for $r < r_1$, are of course more important, but have been in a way taken into account by the introduction of the parameter ϵ.

We write for $f(r)$, the expression obtained in the last chapter, namely

$$r.\,f(r) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{\infty} \frac{\epsilon^2 . s.\,\beta^2(s)\,\sin(rs)\,ds}{\lambda - \epsilon\,\beta(s)} \tag{3.3}$$

and obtain from (2.6) the following for

$$(3.4) \qquad r.\alpha(r) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} s\,\beta(s) \sin(rs)\, ds$$

Combining (3.3) and (3.4) we get

$$(3.5) \quad r\{f(r)+\epsilon\alpha(r)\} = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \left\{ \frac{\epsilon^2 \beta^2(s)}{\lambda - \epsilon\beta(s)} + \epsilon\beta(s) \right\} s.\sin(rs)\, ds$$

$$= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{\epsilon^2\beta^2(s) + (\lambda - \epsilon\beta(s))\epsilon\beta(s)}{\lambda - \epsilon\beta(s)} s.\sin(rs)\, ds$$

$$= \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \frac{\lambda\epsilon s.\beta(s)\sin(rs)\, ds}{\lambda - \epsilon\beta(s)}$$

The form for $f(r)$ as given by equation (3.3) suggests immediately an expansion in powers of the density; in fact for gases where $|\lambda - \epsilon\beta(s)| > 0$ for all real s, such an expansion is permissible, and leads to the following result:

$$(3.6) \quad p = n_1 kT \left\{ 1 - \frac{\beta(0)}{2\lambda} - \sum_{\nu=2}^{\infty} \frac{\nu\epsilon^\nu}{2(2\pi)^{\nu/2}\lambda^\nu} \int_{-\infty}^{\infty} \frac{\beta(s)^{\nu+1}\, s^2\, ds}{\nu+1} \right\}$$

An exact development of the equation of state as powers series in the density was made first by Ursell [6], later improved by Mayer [5], Born and Fuchs [7] and given a quantum generalization by Kahn [8]. The result may be written as follows

$$(3.7) \quad p = n_1 kT \left\{ 1 - \sum_{s=1}^{\infty} \frac{s}{s+1} \beta_s n_1^s \right\}$$

so that the quantities $-\frac{s}{s+1}\beta_s$ are the so-called virial coefficients. The β_s are rather complicated integrals and so far analytic expressions have been found only for the first three [13].

Mayer has shown[5] that the equation (3.7) does not describe the liquid phase, simply because the infinite series become divergent on approaching the point of condensation. The same thing happens to (3.6) when the transcendental equation $\beta(z) = \lambda/\epsilon$ first has a real root and so it is clearly seen why the infinite series in (3.7) diverges. At the exact point where this divergence occurs however, detailed calculations do not confirm that it happens at the density of the saturated vapour. The point of divergence is found as separating the metastable states of the liquid from those of the gas.

One should conclude accordingly, that a different method of expansion is required if one wishes to cover the liquid as well as the gas region. For this purpose it is convenient to consider the complex roots z_u in the upper half of the z-plane of the equation $\beta(z) = \lambda/\epsilon$, and use instead of (3.3) the alternative expression (3.5) for $f(r)$.

It follows from our definition (2.20) that the conditions

(a) $\beta(z)$ reduces to $\beta(r)$ for $z = r$ real, and

(b) $\beta(z) \to 0$ as $|z| \to \infty$, uniformly with respect to arg z, in the upper half of the z-plane, are satisfied. By applying a well known theorem of the calculus of residues, (3.5) becomes

$$(3.8)\qquad r f(r) = -\epsilon\,\alpha(r).r - (2\pi)^{1/2}\frac{\lambda^2}{\epsilon}\sum_u \frac{z_u}{\beta'(z_u)}\,e^{ir z_u}$$

Inserting (3.8) and (3.2) in (3.1) we obtain after some calculation,

$$(3.9)\qquad p = n_1 kT\Big\{1 - \frac{\beta(0)}{2\lambda} + \frac{\epsilon}{4(2\pi)^{1/2}\lambda}\int_{-\infty}^{\infty}\beta^2(r)\,r^2\,dr + \\ + \frac{2}{3}\frac{\lambda}{\epsilon}\sum_u \frac{z_u}{\beta'(z_u)}\int_0^\infty r.\alpha(r)\,e^{ir z_u}\,dr \\ + \frac{i\lambda}{3\epsilon}\sum_u \frac{z_u^2}{\beta'(z_u)}\int_0^\infty r^2.\alpha(r)\,e^{ir z_u}\,dr$$

Equation (3.9) holds equally for the liquid and the gas. The difference between them arises from the fact that in the case of the liquid there are two real roots which are not included in the u-summation in (3.9).

Let us discuss what happens for temperature below the critical temperature. In figure 2 we have plotted the function $\beta(r)$ for a certain temperature T sufficiently low.

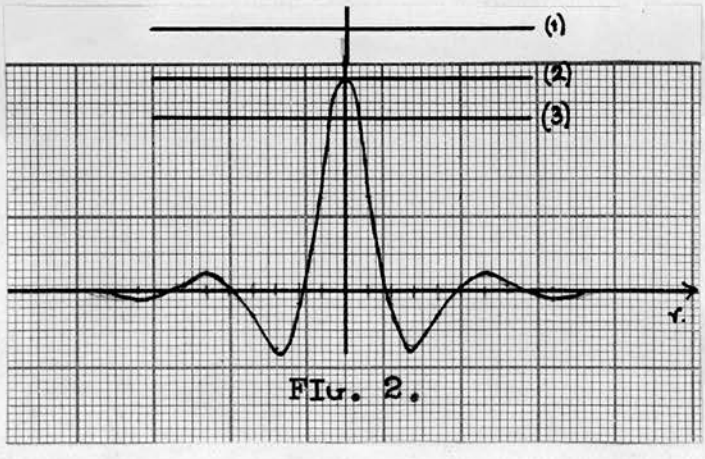


FIG. 2.

For low densities λ/ϵ exceeds the upper bound of $\beta(r)$, (case (1) in figure 2) and the fundamental equation has no real roots. We interpret this as the

region of the gas. If we now increase the density, keeping the temperature constant, we reach a certain density, (case (2) in figure 2) at which we have two coincident real roots. This point we interpret as separating the metastable states of the liquid from those of the gas. If the density is increased still more, one has two real roots (case (3) in figure 2) which of course are not included in the u-summation of (3.9). We interpret this region for which equation $\beta(z) = \lambda/\epsilon$ has two real roots, as the liquid phase.

For higher temperatures the upper bound of $\beta(r)$, which always occurs at the point $r = 0$, becomes so small that only at exceedingly high densities the equation $\beta(z) = \lambda/\epsilon$ will have real roots. Therefore the liquid region can never be reached.

Equation (3.9) is our final equation of state. It can not be put in the form

$$(3.10) \quad p = n_1 kT \left\{ 1 - \frac{\beta(0)}{2\lambda} + \frac{\epsilon}{4(2\pi)^{1/2}\lambda} \int_{-\infty}^{\infty} r^2 \beta^2(r)\, dr + \right.$$
$$\left. + \frac{(2\pi)^{1/2} i\, \lambda}{3\epsilon} \sum_{w} \left(\frac{\lambda z_w^2}{\epsilon \beta(z_w)} + \frac{z_w^3}{3} \right) \right\}$$

as was given in Green's original paper [2] because

$$\int_0^{\infty} r \cdot \alpha(r)\, e^{irz_w}\, dr \neq \int_{-\infty}^{\infty} r \cdot \alpha(r)\, e^{irz_w}\, dr$$

for all z_w complex in the upper half of the complex plane.

In some previous considerations we mentioned the

fact that the parameter ϵ ,which was introduced to average the function $f(r)$,is not a constant,but a function of temperature and density.

If we choose λ/ϵ as a parameter,equation (3.8), after multiplication by $r.\ \alpha(r)$,can be brought into the form

$$(3.11)\quad \frac{\int_0^\infty r^2.\alpha(r)\,f(r)\,dr}{\int_0^\infty r^2\alpha(r)\,dr.}\cdot\int_0^\infty r^2.\alpha(r)\,dr = -\epsilon\int_0^\infty r^2.\alpha_{(r)}^2\,dr - \epsilon(2\pi)^{3/2}\left(\frac{\lambda}{\epsilon}\right)^2\sum_u \frac{z_u}{\beta^1(z_u)}\int_0^\infty r.\alpha(r)\,e^{ir z_u}\,dr$$

The first factor in the left hand-side is by definition equal to $(\epsilon-1)$. Hence we obtain

$$(3.12)\quad \epsilon = \frac{\int_0^\infty r^2.\alpha(r)\,dr}{\int_0^\infty r^2\alpha(r)\,dr + \int_0^\infty r^2.\alpha_{(r)}^2\,dr + (2\pi)^{3/2}\left(\frac{\lambda}{\epsilon}\right)^2\sum_u \frac{z_u}{\beta^1(z_u)}\int_0^\infty r.\alpha(r)\,e^{ir z_u}\,dr.}$$

It is obvious from (3.8) that at high temperatures and low densities $\epsilon \to 1$ since $f(r)$ is actually equal to zero.

For comparatively low temperatures and high densities ϵ will not equal to 1 since $f(r)$ may take considerable high values. Detailed calculations made for Argon,as will shown in chapter VII,confirm this argument. For this gas at temperatures near the critical temperature $\epsilon = 0.60$,and remains constant practically for all values of density. For the same gas and a temperature $T = 130^\circ$ K , $\epsilon = 0.46$.

CHAPTER IV. THE FREE ENERGY.

In a previous chapter we have found an explicit expression for the pressure p. It is now possible to obtain a new expression for the free energy A by intagrating the partial differential equation:

$$\frac{\partial}{\partial V}\left(\frac{A}{T}\right) = -\frac{p}{T} \tag{4.1}$$

As we observed in chapter III, the parameter ϵ can no longer be considered a constant, because in fact it is a function of temperature and density. Numerical evaluation, which we give in chapter VII, shows that its dependence on density is quite negligible and it may, therefore, be considered constant if we keep the temperature constant.

If we now write

$$\varphi_u = \int_0^\infty r \cdot \alpha(r)\, e^{ir z_u}\, dr \tag{4.2}$$

and

$$\psi_u = \int_0^\infty r^2 \cdot \alpha(r)\, e^{ir z_u}\, dr \tag{4.3}$$

equation of state (3.8) can be written

$$p = n_1 RT \left\{ 1 - \frac{\beta(0)}{2\lambda} + \frac{\epsilon}{4(2\pi)^{1/2}\lambda} \int_{-\infty}^{\infty} r^2 \cdot \alpha^2(r)\, dr + \right.$$

$$\left. + \frac{\lambda}{3\epsilon} \sum_u \frac{z_u}{\beta'(z_u)} \left\{ 2 z_u \cdot \varphi_u + z_u^2 \cdot \frac{\partial \varphi_u}{\partial z_u} \right\} \right\} \tag{4.4}$$

since, according to (4.2) and (4.3) we have

(4.5) $$\frac{\partial \varphi_u}{\partial z_u} = i\,\varphi_u$$

From equation $\beta(z) \rightleftarrows \lambda/\epsilon$, it follows since we assume ϵ to be constant with respect to density, that

(4.6) $$\frac{\partial z_u}{\partial V} = \frac{\lambda n_1}{\epsilon N \beta'(z_u)}$$

Hence, (4.1) is integrable and it is easy to obtain:

(4.7) $$A = -\frac{NkT}{2\lambda}\left\{\beta(0) - \frac{\epsilon}{2(2\pi)^{1/2}}\int_{-\infty}^{\infty} r^2 \alpha^2(r)\,dr + \right.$$

$$\left. + \frac{2\lambda}{3}\sum_u (z_u^2 \cdot \varphi_u)\right\} + NkT \log n_1 + \chi(T)$$

$\chi(T)$ being a constant of integration. By taking λ sufficiently large (4.7) reduces to

(4.8) $$(A - NkT \log n_1)_{n_1 \text{ small}} = \chi(T)$$

which gives for $\chi(T)$ the well known result

(4.9) $$\chi(T) = -\frac{3}{2} NkT \log T$$

Inserting (4.9) in (4.7) we obtain finally for A, the expression

(4.10) $$A = -\frac{NkT}{2\lambda}\left\{\beta(0) - \frac{\epsilon}{2(2\pi)^{1/2}}\int_{-\infty}^{\infty} r^2 \alpha^2(r)\,dr + \right.$$

$$\left. + \frac{2\lambda}{3}\sum (z_u^2 \cdot \varphi_u)\right\} + NkT \log n_1 - \frac{3}{2} NkT \log T.$$

(4.10) is of course approximate. It contains not only the approximations which were used for obtaining the

pressure p, but is obtained under the assumption that ϵ is only a function of temperature.

CHAPTER V. THE SOLUTION OF THE TRANSCENDENTAL EQUATION

1. The algebraic equation.

We have seen how by using an appropiate expansion for the function $r \cdot \alpha(r)$ we have been able to define the analytic function $\beta(z)$; here we shall be concerned with the solution of the fundamental equation

$$\beta(z) = \lambda/\epsilon \tag{5.1}$$

For real values of the variable r, $\beta(r)$ satisfies by definition equation (2.6),i.e.

$$r \cdot \beta(r) = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} s \cdot \alpha(s) \sin(rs)\, ds \tag{5.2}$$

where $\alpha(s)$,to be considered as a known function,is given by

$$\alpha(s) = e^{-\phi(s)/kT} - 1 \tag{5.3}$$

We assume now that $s \cdot \alpha(s)$ admits an expansion of the type

$$s \cdot \alpha(s) = \sum_{k=-n}^{n} c_k e^{is\xi_k} \tag{5.4}$$

ξ_k being an arbitrary complex number in the upper half of the z-plane. In what follows the number n in this sum shall be considered finite. Inserting (5.4) in (5.2) and performing the integration (see chapterII) we obtain

$$\beta(r) = -\frac{2}{(2\pi)^{1/2}} \sum_{k=-n}^{n} \frac{c_k}{\xi_k^2 - r^2} \tag{5.5}$$

We now extend the definition (5.5) for complex values z of r. Then (5.1) becomes

$$(5.6)\qquad \sum_{k=-n}^{n} \frac{C_k}{\xi_k^2 - z^2} = -\frac{(2\pi)^{1/2}}{2}\,\frac{\lambda}{\epsilon}$$

which is an algebraic equation of order 4n+2.

If we write

$$(5.7)\qquad C_k = \frac{(2\pi)^{1/2}\,\lambda\, C_k}{2\epsilon}$$

(5.6) becomes simply:

$$(5.8)\qquad z^{4n+2} - P_1 z^{4n} + P_2 z^{4n-2} - \cdots\cdots \pm P_{2n+1} = 0$$

where

$$(5.9)\qquad P_j = \Pi_j + \sum_{k=-n}^{n} C_k \Pi_{j-1}^{(k)} \qquad (j = 1, 2, \ldots\ldots, 2n+1)$$

and the following notation has been introduced:

$$(5.10)\quad \begin{cases} \Pi_1 = \xi_0^2 + \xi_{-1}^2 + \xi_1^2 + \cdots + \xi_{-n}^2 + \xi_n^2 \quad ; \quad \Pi_0^{(k)} = 1 \\ \Pi_2 = \xi_0^2\xi_{-1}^2 + \xi_0^2\xi_1^2 + \cdots\cdots + \xi_{-n}^2\xi_n^2 \quad ; \quad \Pi_1^{(k)} = \xi_0^2 + \xi_1^2 + \cdots + \xi_{-(k-1)}^2 + \xi_{-k}^2 + \cdots + \xi_n^2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \Pi_{2n+1} = \xi_0^2\xi_1^2\xi_{-1}^2 \cdots \xi_n^2\xi_{-n}^2 \quad ; \quad \Pi_{2n}^{(k)} = \xi_0^2 \cdot \xi_1^2 \cdot \xi_{-1}^2 \cdots \xi_{k-1}^2 \xi_{-k}^2 \xi_{k+1}^2 \cdots \xi_n^2 \end{cases}$$

2. The expansion of the function $s \cdot \alpha(s)$.

In the preceding section of this chapter we have assumed that

$$s \cdot \alpha(s) = \sum_{k=-n}^{n} c_k e^{i s \xi_k} \tag{5.4}$$

ξ_k being of the form:

$$\xi_k = i\alpha_k + \beta_k \quad , \quad \alpha_k > 0 \qquad (k = -n, \dots -1, 0, 1, \dots n) \tag{5.11}$$

and $$\beta_k = -\beta_{-k}$$

We specialize the formulae by assuming α_k independent of k, and choose

$$\alpha_k = \alpha > 0$$

in such a way that

$$s \cdot \alpha(s) \to 0 \qquad \text{for} \quad s > s_0$$

From (5.4) we obtain:

$$\psi(s) = s \cdot \alpha(s) e^{s\alpha} = \tag{5.12}$$

$$= c_0 + \sum_{k=1}^{n} \{ (c_k + c_{-k}) \cos s\beta_k + i (c_k - c_{-k}) \sin s\beta_k \}$$

If α is properly chosen, ψ becomes almost zero for $s = s_0$. Then (5.12) can be expanded as an ordinary Fourier series in the interval $0 \le s \le s_0$, and has approximately

$$\psi(s) = a_0 + \sum_{k=1}^{n} (a_k \cos \theta k + b_k \sin \theta k) \tag{5.13}$$

Comparing (5.13) with (5.12) one has

(5.14) $a_0 = c_0 \quad , \quad c_k + c_{-k} = a_k \quad , \quad i(c_k - c_{-k}) = b_k$

and

(5.15) $\beta_k = \gamma \cdot k \quad , \quad \gamma = \frac{2\pi}{s_0}$

We see clearly that by a fair adjustment of the value of α ,the expansion represents our function, provided we take n conveniently large.

These formulae can be applied now in the following way: as the potential function $\phi(s)$ tends to zero for $s \to \infty$,the function $\alpha(s)$ tends sharply to zero. One can now choose a value of the constant α into abcisa $s = s_0$ in such a way that the function $s.\alpha(s)$ is small enough to be neglected for all $s > s_0$, and $\psi(s)$ becomes almost zero for $s = s_0$. Then one can expand the function $\psi(s)$ in a Fourier series and take the first $2n+1$ terms of (5.13). After numerical evaluation of the coefficients a_k, b_k one finds the constant c_k's from (5.14),while β_k is determined by s_0 with the help of (5.15). The constants ξ_k are of the form $\xi_k = i\alpha \pm \gamma \cdot k$, $\gamma = 2\pi/s_0$ $(k = 0,1,2,\ldots,n)$. Hence one calculates the quantities Π_j from (5.10) (for which in the next section will be given reccurrence formulae). Then from (5.9) (with the help of (5.1)) one obtains the coefficients P_j of the algebraic equation (5.8),the roots of which are determining the thermodynamical properties

as were discussed in chapter III.

3. Reccurrence formulae for the calculation of the coefficients of the algebraic equation.

According to our notation (5.10), it follows:

$$\Pi_1^{(k)} = \Pi_1 - \xi_k^2 \qquad (k=-n,..-1,0,1,...n) \tag{5.16}$$

and in general

$$\Pi_j^{(k)} = \Pi_j - \xi_k^2 \Pi_{j-1}^{(k)} \tag{5.17}$$

Both (5.16) and (5.17) can be simply expressed in the form:

$$\Pi_j^{(k)} = \Pi_j - \xi_k^2 \Pi_{j-1} + \xi_k^4 \Pi_{j-2} - \xi_k^6 \Pi_{j-3} \cdots \pm \xi_k^{2j} \tag{5.18}$$

On the other hand from (5.10) and (5.15) we obtain for

$$\Pi_1 = -(2n+1)\alpha^2 + 2\gamma^2 \sum_{k=1}^{n} k^2 \tag{5.19}$$

It also follows that

$$\begin{cases} \Pi_2 = \frac{1}{2}\left\{\Pi_1 . \Pi_1 - \sum_{k=-n}^{n} \xi_k^4\right\} \\ \Pi_3 = \frac{1}{3}\left\{\Pi_1 . \Pi_2 - \sum_{k=-n}^{n} \Pi_1^{(k)} \xi_k^4\right\} \\ \Pi_4 = \frac{1}{4}\left\{\Pi_1 . \Pi_3 - \sum_{k=-n}^{n} \Pi_2^{(k)} \xi_k^4\right\} \\ \cdots\cdots\cdots\cdots\cdots\cdots \end{cases} \tag{5.20}$$

and quite generally

$$(5.21)\qquad \Pi_j = \frac{1}{j}\left\{ \Pi_1 . \Pi_{j-1} - \sum_{k=-n}^{n} \Pi_{j-2}^{(k)} \xi_k^4 \right\}$$

By making use of (5.17) we get for (5.21)

$$(5.22)\qquad \Pi_j = \frac{1}{j}\left\{ \Pi_1 \Pi_{j-1} - \Pi_{j-2} \sum_{k=-n}^{n} \xi_k^4 + \Pi_{j-3} \sum_{k=-n}^{n} \xi_k^6 - \cdots\cdots \pm \sum_{k=-n}^{n} \xi_k^{2j} \right\}$$

Finally, from (5.11) and (5.15) it follows

$$(5.23)\qquad \sum_{k=-n}^{n} \xi_k^{2j} = (-1)^j (2n+1)\alpha^{2j+1} + 2\left\{ \binom{2j}{2j} \gamma^{2j} . \alpha^0 \sum_{k=1}^{n} k^{2j} - \binom{2j}{2j-2} \gamma^{2j-2} \alpha^2 \sum_{k=1}^{n} k^{2j-2} + \binom{2j}{2j-4} \gamma^{2j-4} \alpha^4 \sum_{k=1}^{n} k^{2j-4} - \cdots\cdots \pm \binom{2j}{2} \gamma^2 . \alpha^{2j-2} \sum_{k=1}^{n} k^2 \right\}$$

We see clearly now how to proceed. By means of equation (5.23) we calculate all the $\sum_{k=-n}^{n} \xi_k^{2j}$ $(j=1,2,\ldots,n)$. Then from (5.22) by putting $j=2$, $j=3$, $\ldots\ldots$, $j=2n+1$ succesively, we calculate all the Π_j. The $\Pi_j^{(k)}$ can then immediately obtained from (5.17).

CHAPTER VI. THE EQUATION OF STATE IN TERMS OF THE EXPANSION.

In chapter III we obtained the equation of state, namely

$$(6.1)\quad p = n_4 k T \left\{ 1 - \frac{\beta(0)}{2\lambda} + \frac{\epsilon}{4(2\pi)^{1/2}\lambda} \int_{-\infty}^{\infty} r^2 \alpha(r)^2 \, dr + \right.$$
$$+ \frac{2\lambda}{3\epsilon} \sum_u \frac{z_u}{\beta'(z_u)} \int_0^{\infty} r \cdot \alpha(r) e^{irz_u} dr$$
$$\left. + \frac{i\lambda}{3\epsilon} \sum_u \frac{z_u^2}{\beta'(z_u)} \int_0^{\infty} r^2 \cdot \alpha(r) e^{irz_u} dr \right\}$$

We shall now express (6.1) in terms of the coefficients of the expansion (5.4), i.e. in terms of the c_k's and ξ_k's.

We obtain, remembering that

$$(6.2)\quad \nu \alpha(r) = \sum_{k=-n}^{n} c_k e^{ir\xi_k}$$

the following expressions for the terms appearing in (6.1):

$$(6.3)\quad \beta(0) = -\frac{2}{(2\pi)^{1/2}} \sum_{k=-n}^{n} \frac{c_k}{\xi_k^2} \,,$$

$$(6.4)\quad \int_{-\infty}^{\infty} r^2 \alpha(r)^2 \, dr = -2 \sum_{k,s=-n}^{n} \frac{c_k c_s}{i(\xi_k + \xi_s)} \,,$$

$$(6.5)\quad \int_0^{\infty} r \cdot \alpha(r) e^{irz_u} dr = i \sum_{k=-n}^{n} \frac{c_k}{(\xi_k + z_u)}$$

and

$$(6.6)\qquad \int_0^\infty r^2 \cdot \alpha(r)\, e^{irz_u}\, dr = \sum_{k=-n}^{n} \frac{c_k}{(\xi_k + z_u)^2}$$

From equation (2.15) for $\beta(z)$ it follows

$$(6.7)\qquad \frac{\beta'(z_u)}{z_u} = -\frac{4}{(2\pi)^{1/2}} \sum_{k=-n}^{n} \frac{c_k}{(\xi_k^2 - z_u^2)^2}$$

Since the summation in (6.1) is extended over the complex roots z_u, in the upper half plane, it follows from (5.8) that

$$(6.8)\qquad \begin{cases} z_0 = i\omega_0 \\ z_u = s_u + i t_u \\ z_{-u} = -s_u + i t_u \end{cases}$$

where ω_0, s_u and t_u are real positive numbers.

We introduce the following notation,

$$(6.9)\qquad \begin{cases} i\sum_{k=-n}^{n} \frac{c_k}{\xi_k + z_0} = A_0 \\ i\sum_{k=-n}^{n} \frac{c_k}{\xi_k + z_u} = A_u + i B_u \\ i\sum_{k=-n}^{n} \frac{c_k}{\xi_k + z_{-u}} = A_u - i B_u \end{cases} \quad (u = 1, 2, \ldots n)$$

$$(6.10)\qquad \begin{cases} \sum_{k=-n}^{n} \frac{c_k}{(\xi_k + z_0)^2} = A_0' \\ \sum_{k=-n}^{n} \frac{c_k}{(\xi_k + z_u)^2} = A_u' + i B_u' \\ \sum_{k=-n}^{n} \frac{c_k}{(\xi_k + z_{-u})^2} = A_u' - i B_u' \end{cases} \quad (u = 1, 2, \ldots n)$$

and

$$-\frac{4}{(2\pi)^{1/2}}\sum_{k=-n}^{n}\frac{c_k}{(\xi_k^2-z_0^2)^2}=A_0''$$

$$(6.11)\qquad \left.\begin{aligned}-\frac{4}{(2\pi)^{1/2}}\sum_{k=-n}^{n}\frac{c_k}{(\xi_k^2-z_u^2)^2}&=A_u''+iB_u''\\ -\frac{4}{(2\pi)^{1/2}}\sum_{k=-n}^{n}\frac{c_k}{(\xi_k^2-z_{-u}^2)^2}&=A_u''-iB_u''\end{aligned}\right\}(u=1,2,\dots n)$$

Hence, the last two terms in (6.1) become, according to (6.5), (6.6) and (6.9), (6.10) and (6.11)

$$(6.12)\qquad \frac{2\lambda}{3\epsilon}\sum_u\frac{z_u}{\beta'(z_u)}\int_0^\infty r\cdot\alpha(r)\,e^{irz_u}\,dr=\frac{2\lambda}{3\epsilon}\left(\frac{A_0}{A_0''}+2\sum_{u=1}^{n}\frac{A_uA_u''+B_uB_u''}{A_u''^2+B_u''^2}\right)$$

and

$$\frac{i\lambda}{3\epsilon}\sum\frac{z_u^2}{\beta'(z_u)}\int_0^\infty r^2\cdot\alpha(r)\,e^{irz_u}\,dr=$$

$$(6.13)\qquad =-\frac{\lambda}{3\epsilon}\left\{\frac{A_0'}{A_0''}\omega_0+2\sum_{u=1}^{n}\frac{s_u(A_u'B_u''-A_u''B_u')+t_u(A_u'A_u''+B_u'B_u'')}{A_u''^2+B_u''^2}\right\}$$

respectively.

CHAPTER VII. APPLICATION. THE EQUATION OF STATE FOR ARGON.

1. The expansion of $S.\alpha(s)$ for $T=150°$ K.

In chapter V, section 2 we explained how to proceed to calculate the coefficients in the expansion of the function $S.\alpha(s)$. In order to tabulate the function $\psi(s)$ we assume the potential function $\phi(s)$ to be a known function. We adopt for this purpose Lennard-Jones potential[11], namely

$$\phi(s) = \frac{a}{s^6} - \frac{b}{s^{12}} \tag{7.1}$$

For Argon the two constants a and b have the values

$$a = 1.03 \times 10^{-10} \text{ ergs } \text{Å}^6$$
$$b = 1620 \times 10^{-10} \text{ ergs } \text{Å}^{12} \tag{7.2}$$

respectively.

Figure 3 shows $\phi(s)$.

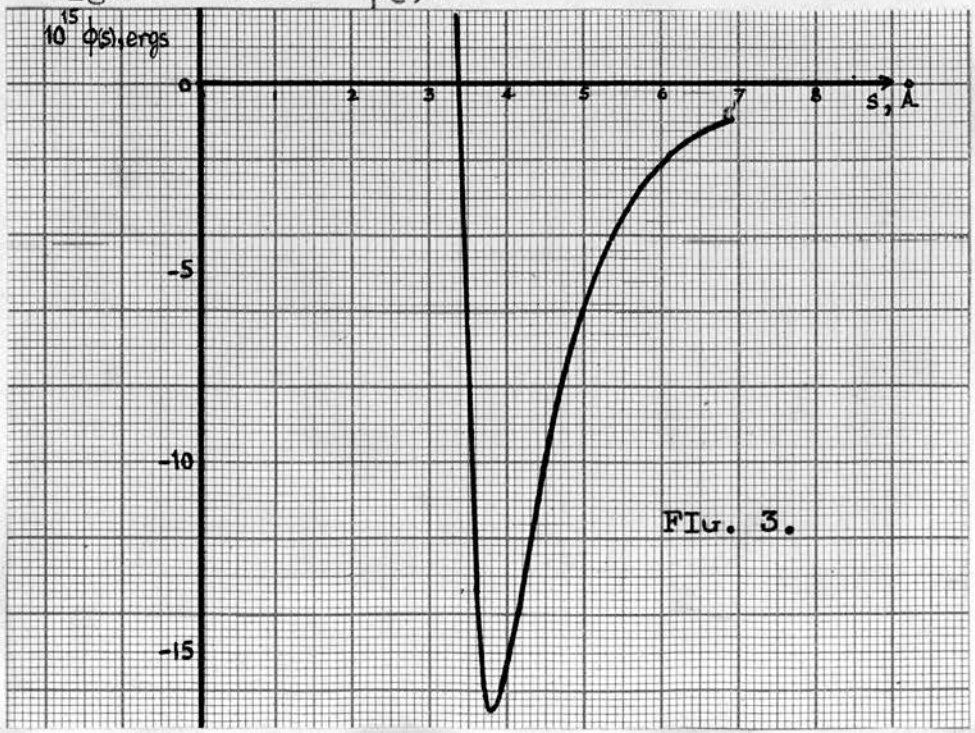


FIG. 3.

The minimun of $\phi(s)$ takes place for a value s_1 of s given by

$$s_1 = \sqrt[6]{\frac{2b}{a}} = 3.83\,\text{Å} \tag{7.3}$$

for which

$$\phi(s_1) = -16.5 \times 10^{-15}\ \text{ergs} \tag{7.4}$$

In figures 4 , 5 and 6 we have plotted the functions $\alpha(s) = e^{-\phi(s)/kT} - 1$, $s.\alpha(s)$ and $\psi(s) = s.\alpha(s)\, e^{\alpha.s}$ respectively, where α has been chosen equal to $0.3\,\text{Å}^{-1}$, and found to be very suitable to satisfy both conditions, namely that $s.\alpha(s) \to 0$ for $s > s_0$ and $\psi(s_0) \sim 0$. The value for s_0 has been taken equal to 7.2 Å. Hence $\gamma = 2\pi/s_0 = 0.872\ \text{Å}^{-1}$

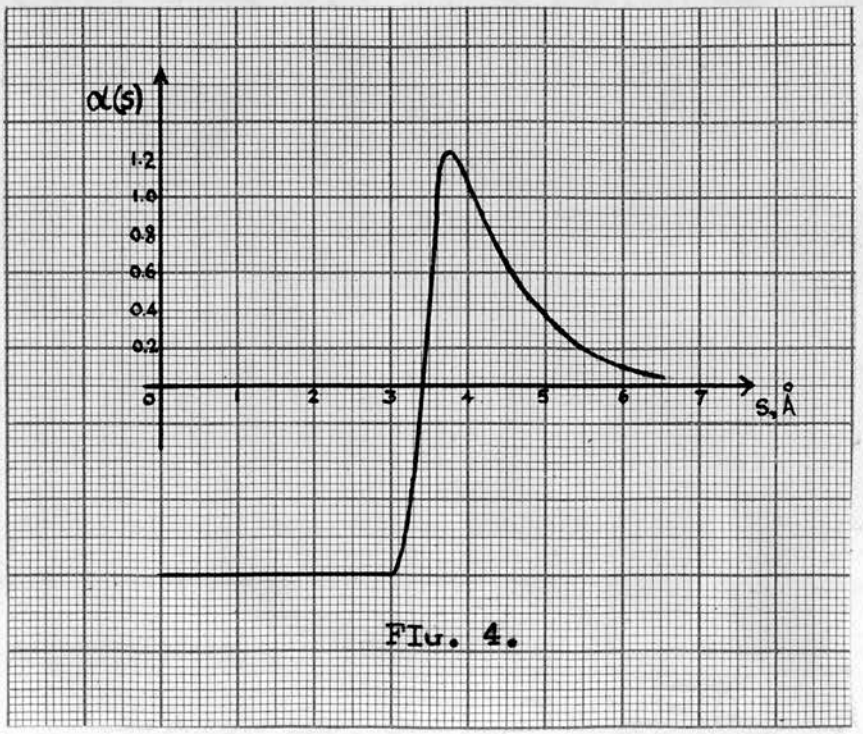


Fig. 4.

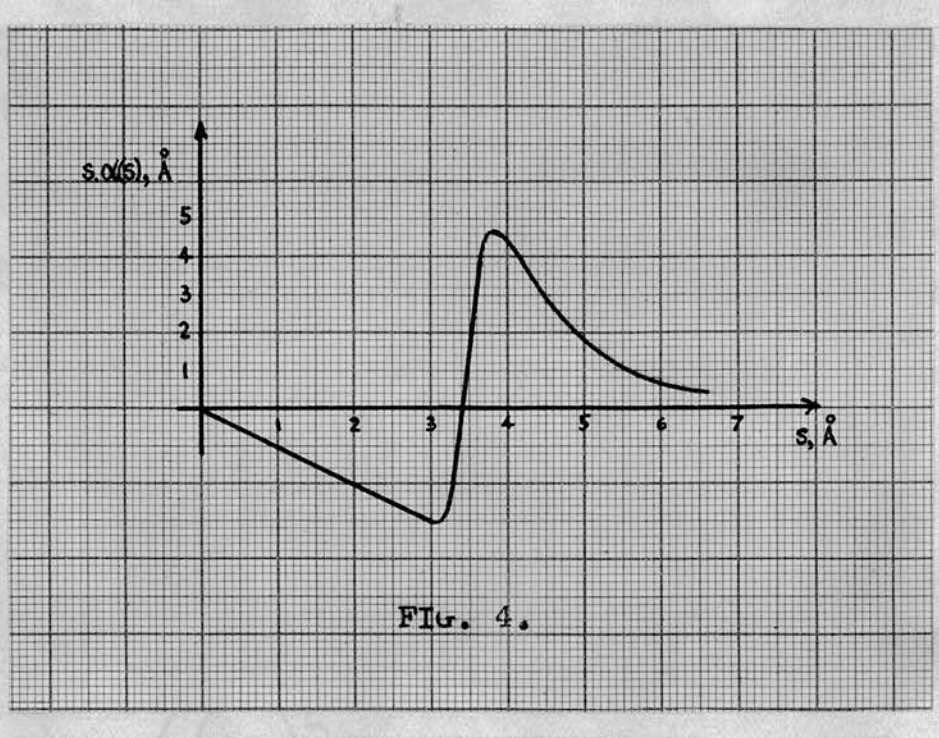


FIG. 4.

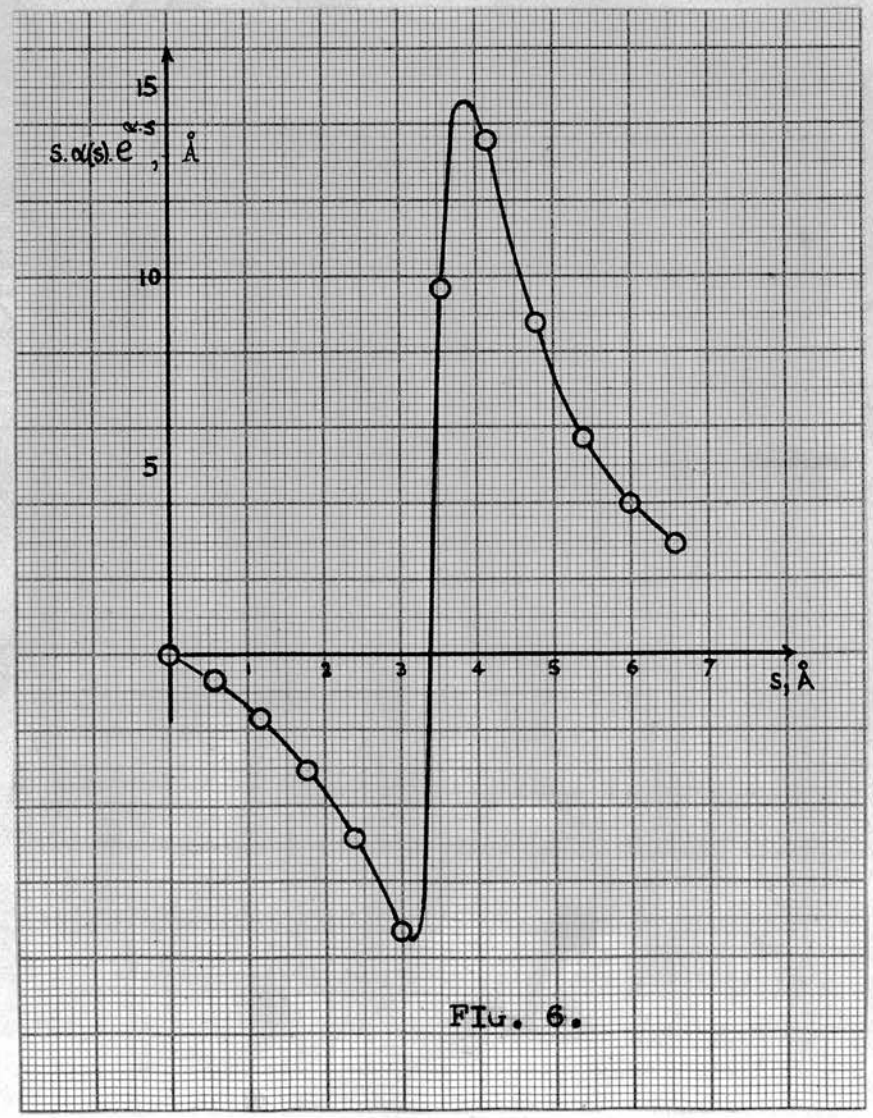


FIG. 6.

Next step is concerned with the evaluation of the coefficients C_k's in the expansion

$$(7.5) \qquad S.\alpha(s) = \sum_{k=-n}^{n} C_k e^{is\xi_k}$$

where we shall take n=6. This gives

$$(7.6) \qquad \psi(s) = a_0 + \sum_{k=1}^{6} (a_k \cos\theta k + b_k \sin\theta k)$$

Here the a_0, a_k's and b_k's are determined by means of a Fourier analysis[12]. We have fixed 12 points of the curve $\psi(s)$ as given in figure 6, equally spaced in the interval $0 \le s \le s_0 = 7.2$ Å.

Fourier analysis form, which we give below, shows the actual calculation for T=150° K.

FOURIER ANALYSIS FORM.

Harmonic Analysis of $S.\alpha(s)\, e^{\alpha.s}$ T = 150° K. Period.....

θ.				
0°	u_0	000		
30°	u_1	-071		
60°	u_2	-174		
90°	u_3	-311		
120°	u_4	-491		
150°	u_5	-737		
180°	u_6	965		
210°	u_7	1360		
240°	u_8	875		
270°	u_9	573		
300°	u_{10}	399		
330°	u_{11}	291		

(u_0 to u_6)	000	-071	-174	-311	-491	-737	965
(u_{11} to u_7)		291	399	573	875	1360	
Sums (v_0 to v_6)	000	219	225	262	384	623	965
Diffs. (w_1 to w_5)		-363	-573	-884	-1366	-2097	

(v_0 to v_3)	000	219	225	262
(v_6 to v_4)	965	623	384	
Sums (p_0 to p_3)	965	842	609	262
Diffs. (q_0 to q_2)	-965	-404	-159	

(w_1 to w_3)	-363	-573	-884	
(w_5 to w_4)	-2097	-1366		
Sums (r_1 to r_3)	-2460	-1939	-884	
Diffs. (s_1 to s_2)	1734	793		

	p_1=842	p_2=609	q_2=-159	r_1=-2460
(½ line above)	h_1=421	h_2=304	l_2=079	m_1=-1230

	q_1=404	r_2=1939	s_1=1734	s_2=793
(0·866 × line above)	l_1=349	m_2=1679	n_1=1501	n_2=687

	p_0=965 p_1=842 p_2=609 p_3=262	q_0=965 l_1=349 l_2=079	p_0=965 h_1=421 p_3=262 h_2=304	p_0=965 p_3=262 h_1=421 h_2=304	m_1=-1230 m_2=-1679 r_3=884 159	q_0=965 q_2=159	n_1=1501 n_2=687	r_1=-2460 r_3=-884	
Sum of 1st column.	1574	-1044	1227	1386	-2114				
Sum of 2nd column	1104	-349	725	566	-1679				
Sum	2678 = $12a_0$	-1393 = $6a_1$			-3793 = $6b_1$			2188 = $6b_2$	
Diff.	470 = $12a_6$	-695 = $6a_5$	504 = $6a_4$	820 = $6a_2$	-435 = $6b_5$	-806 = $6a_3$	814 = $6b_4$		-1576 = $6b_3$

We get from it, the following values for the a_k's (expressed in A units) :

$a_0 = 2.231$	$a_1 = -2.321$	$b_1 = -6.321$
	$a_2 = 1.366$	$b_2 = 3.646$
	$a_3 = -1.343$	$b_3 = -2.626$
	$a_4 = 0.836$	$b_4 = 1.356$
	$a_5 = -1.158$	$b_5 = -0.725$
	$a_6 = 0.391$	$b_6 = 0.000$

2. <u>The form of $\beta(r)$. Approximate calculation of the first three roots of the algebraic equation as a function of density.</u>

In chapter II we obtained an explicit expression for $\beta(r)$,namely

(7.7) $$\beta(r) = -\frac{2}{(2\pi)^{1/2}} \sum_{k=-6}^{6} \frac{C_k}{(\xi_k^2 - r^2)}$$

In figure 7 we have plotted $\beta(r)$ for T=150° K.

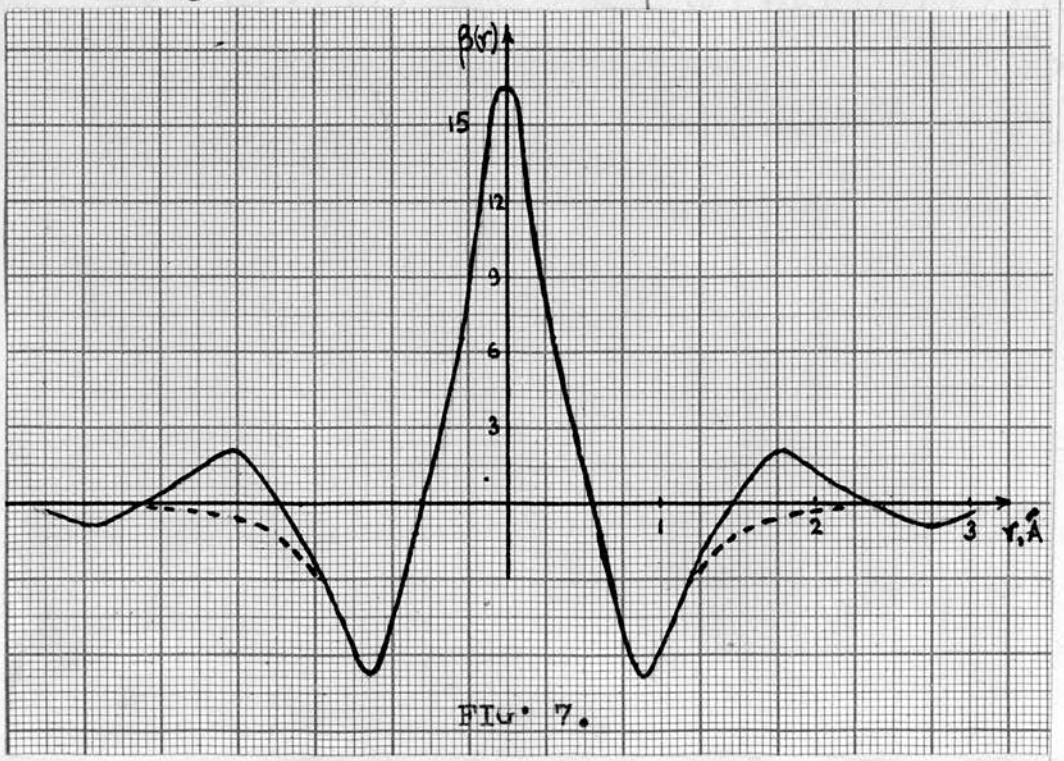


FIG. 7.

The dashed curve in figure 7 represents the actual function $\beta(r)$ from which we have calculated the first three roots. For this case, equation (5.8) reduces to:

$$(7.8) \qquad z^6 - P_1 z^4 + P_2 z^2 - P_3 = 0$$

where the P_j's are given according to (5.9) by

$$P_1 = \left(1.250 - 0.0718/\lambda/\epsilon\right) \text{Å}^{-2}$$
$$P_2 = 0.602 + 3.949/\lambda/\epsilon \ \text{Å}^{-4}$$
$$P_3 = -0.065 + 1.157/\lambda/\epsilon \ \text{Å}^{-6}$$

since it follows from (5.19), (5.20), (5.16) and (5.7) that

$$\Pi_1 = 1.250 \ \text{Å}^{-2} \quad \Pi_1^{\circ} = 1.34 \ \text{Å}^{-2} \quad \Pi_2^{(\circ)} = 0.722 \ \text{Å}^{-4}$$
$$\Pi_2 = 0.602 \ \text{Å}^{-4} \quad \Pi_1^{(1)} = (0.58 - 0.523\,i)\text{Å}^{-2}; \ \Pi_2^{(1)} = (-0.059 + 0.047\,i)\text{Å}^{-4}$$
$$\Pi_3 = -0.065 \ \text{Å}^{-6} \quad \Pi_1^{(-1)} = 0.58 + 0.523\,i)\text{Å}^{-2}; \ \Pi_2^{(-1)} = (-0.059 - 0.047\,i)\text{Å}^{-4}$$

and

$$\sum c_k = -0.090 \ \text{Å}; \quad 2/(2\pi)^{1/2} \sum c_k = -0.072 \ \text{Å}$$
$$\sum c_k \Pi_1^{(k)} = 4.949 \ \text{Å}^{-1}; \quad 2/(2\pi)^{1/2} \sum c_k \Pi_1^{(k)} = 3.950 \ \text{Å}^{-1}$$
$$\sum c_k \Pi_2^{(k)} = 1.450 \ \text{Å}^{-3}; \quad 2/(2\pi)^{1/2} \sum c_k \Pi_2^{(k)} = 1.157 \ \text{Å}^{-3}$$

The c_k's have been obtained from the a_k's and b_k's calculated in the last section by means of the following equations

$$c_k = \frac{a_k - i b_k}{2} \quad ; \quad c_{-k} = \frac{a_k + i b_k}{2}$$

Table 1 gives the final result. Here the notation is the same as that introduced in chapter VI.

Table 1

λ/ϵ, Å^3	ω_0, Å^{-1}	s_4, Å^{-1}	t_4, Å^{-1}
10		0.883	0.431
12		0.879	0.411
15		0.876	0.390
16		0.875	0.385
17		0.875	0.381
17.85		0.874	0.377
17.86	0.00	0.874	0.377
18	0.028	0.874	0.376
19	0.069	0.874	0.372
20	0.094	0.874	0.369
21	0.109	0.873	0.366
22	0.124	0.873	0.363
23	0.135	0.873	0.360
24	0.145	0.873	0.358
25	0.153	0.872	0.356
26	0.161	0.872	0.354
28	0.173	0.872	0.350
30	0.184	0.872	0.345
32	0.193	0.872	0.344
34	0.200	0.872	0.341

3. Calculation of the integrals involving the complex roots.

In Table 2 we give detailed calculation for the numerical evaluation of the integral

$$(7.8) \qquad \int_0^\infty r\,\alpha(r)\, e^{irz_0}\, dr = i \sum_{k=-3}^{3} \frac{c_k}{\xi_k + z_0}$$

The summation has been cut off after the third term, since other terms do not give an appreciable contribution. In what follows the notation will be the same as that introduced in chapter VI.

Table 2

λ/ϵ, Å^3	$i\left\{\frac{c_0}{\xi_0+z_0}\right\}$	$i\left\{\frac{c_1}{\xi_1+z_0}+\frac{c_{-1}}{\xi_{-1}+z_0}\right\}$	$i\left\{\frac{c_2}{\xi_2+z_0}+\frac{c_{-2}}{\xi_{-2}+z_0}\right\}$	$i\left\{\frac{c_3}{\xi_3+z_0}+\frac{c_{-3}}{\xi_{-3}+z_0}\right\}$	A_0, Å^2
10					
....					
17.86	7.436	-7.300	2.161	-1.049	1.248
18	6.792	-7.226	2.161	-1.052	0.676
19	6.039	-7.102	2.159	-1.055	0.041
20	5.656	-7.017	2.157	-1.057	-0.261
21	5.447	-6.963	2.155	-1.058	-0.418
22	5.263	-6.910	2.153	-1.059	-0.552
23	5.126	-6.867	2.152	-1.059	-0.648
24	5.012	-6.828	2.150	-1.060	-0.726
25	4.923	-6.796	2.149	-1.061	-0.785
26	4.837	-6.764	2.147	-1.061	-0.841
28	4.711	-6.714	2.145	-1.062	-0.919
30	4.606	-6.669	2.142	-1.062	-0.982
32	4.528	-6.634	2.141	-1.063	-1.028
34	4.457	-6.602	2.139	-1.063	-1.068

In Table 3 we give detailed calculation for the numerical evaluation of the real part of the integral

$$(7.9)\qquad \int_0^\infty r\,\alpha(r)\,e^{ir\xi_1}\,dr = i\sum_{k=-3}^{3}\frac{C_k}{(\xi_k+\xi_1)}$$

Table 3

λ/ϵ, Å^3	$R\{i\frac{C_0}{\xi_0+\xi_1}\}$	$R\{\frac{iC_1}{\xi_1+\xi_1}\}$	$R\{\frac{iC_{-1}}{\xi_{-1}+\xi_1}\}$	$R\{\frac{iC_2}{\xi_2+\xi_1}\}$	$R\{\frac{iC_{-2}}{\xi_{-2}+\xi_1}\}$
10	1.241	-1.769	-1.522	0.711	1.622
12	1.240	-1.780	-1.585	0.713	1.645
15	1.237	-1.790	-1.651	0.714	1.669
16	1.236	-1.794	-1.668	0.715	1.676
17	1.235	-1.795	-1.683	0.715	1.681
17.85	1.234	-1.797	-1.695	0.716	1.686
17.86	1.234	-1.797	-1.695	0.716	1.686
18	1.234	-1.797	-1.697	0.716	1.687
19	1.233	-1.799	-1.709	0.716	1.692
20	1.232	-1.800	-1.719	0.716	1.696
21	1.231	-1.802	-1.731	0.716	1.700
22	1.230	-1.803	-1.739	0.716	1.703
23	1.229	-1.804	-1.747	0.717	1.706
24	1.228	-1.805	-1.755	0.717	1.709
25	1.227	-1.806	-1.762	0.717	1.711
26	1.226	-1.807	-1.768	0.717	1.715
28	1.225	-1.808	-1.780	0.717	1.719
30	1.223	-1.809	-1.790	0.717	1.723
32	1.222	-1.810	-1.799	0.718	1.727
34	1.221	-1.813	-1.807	0.718	1.730

λ/ϵ, Å^3	$R\{\frac{iC_3}{\xi_3+\xi_1}\}$	$R\{\frac{iC_{-3}}{\xi_{-3}+\xi_1}\}$	A_1, Å^2
10	-0.397	-0.782	-0.897
12	-0.398	-0.783	-0.948
15	-0.398	-0.784	-1.002
16	-0.398	-0.785	-1.018
17	-0.398	-0.785	-1.026
17.85	-0.398	-0.785	-1.039
17.86	-0.398	-0.785	-1.039
18	-0.398	-0.785	-1.040
19	-0.398	-0.785	-1.051
20	-0.398	-0.786	-1.060
21	-0.398	-0.786	-1.070
22	-0.398	-0.786	-1.077
23	-0.398	-0.786	-1.084
24	-0.398	-0.787	-1.091
25	-0.398	-0.787	-1.098
26	-0.398	-0.787	-1.102
28	-0.398	-0.787	-1.113
30	-0.398	-0.787	-1.121
32	-0.398	-0.788	-1.129
34	-0.398	-0.788	-1.138

In Table 4 we give detailed calculations for the numerical evaluation ofthe imaginary part of integral (7.9).

Table 4

λ/ϵ, Å^3	$J\{\frac{iC_0}{\xi_0+z_1}\}$	$J\{\frac{iC_1}{\xi_1+z_1}\}$	$J\{\frac{iC_{-1}}{\xi_{-1}+z_1}\}$	$J\{\frac{iC_2}{\xi_2+z_1}\}$	$J\{\frac{iC_{-2}}{\xi_{-2}+z_1}\}$
10	1.499	-0.076	-4.347	0.062	0.583
12	1.534	0.060	-4.461	0.067	0.563
15	1.570	0.043	-4.586	0.072	0.542
16	1.583	0.039	-4.620	0.074	0.536
17	1.588	0.035	-4.651	0.075	0.531
17.85	1.595	0.032	-4.675	0.076	0.527
17.86	1.595	0.032	-4.675	0.076	0.527
18	1.596	0.031	-4.679	0.076	0.527
19	1.603	0.028	-4.704	0.077	0.523
20	1.609	0.025	-4.727	0.078	0.519
21	1.615	0.022	-4.750	0.079	0.516
22	1.620	0.020	-4.769	0.079	0.513
23	1.624	0.018	-4.787	0.080	0.510
24	1.629	0.016	-4.804	0.081	0.507
25	1.633	0.014	-4.820	0.081	0.505
26	1.637	0.012	-4.835	0.082	0.503
28	1.644	0.009	-4.862	0.083	0.499
30	1.650	0.006	-4.887	0.084	0.495
32	1.655	0.003	-4.907	0.084	0.493
34	1.660	0.002	-4.926	0.085	0.490

λ/ϵ, Å^3	$J\{\frac{iC_3}{\xi_3+z_1}\}$	$J\{\frac{C_{-3}}{\xi_{-3}+z_1}\}$	B_1, Å^2
10	-0.109	0.058	-2.178
12	-0.111	0.066	-2.281
15	-0.113	0.074	-2.397
16	-0.114	0.077	-2.425
17	-0.115	0.079	-2.457
17.85	-0.115	0.080	-2.479
1786	-0.115	0.080	-2.479
18	-0.115	0.080	-2.483
19	-0.116	0.082	-2.507
20	-0.116	0.083	-2.528
21	-0.116	0.085	-2.549
22	-0.117	0.086	-2.567
23	-0.117	0.087	-2.584
24	-0.117	0.088	-2.600
25	-0.118	0.089	-2.615
26	-0.118	0.090	-2.629
28	-0.118	0.092	-2.654
30	-0.119	0.093	-2.678
32	-0.119	0.094	-2.696
34	-0.119	0.095	-2.713

In Table 5 we give detailed calculations for the numerical evaluation of the integral

$$(7.10) \qquad \int_0^\infty r^2 \alpha(r)\, e^{irz_0}\, dr = \sum_{k=-3}^{3} \frac{C_k}{(\xi_k + z_0)^2}$$

Table 5

λ/ϵ, Å	$\frac{C_0}{(\xi_0+z_0)^2}$	$\frac{C_1}{(\xi_1+z_0)^2}+\frac{C_{-1}}{(\xi_{-1}+z_0)^2}$	$\frac{C_2}{(\xi_2+z_0)^2}+\frac{C_{-2}}{(\xi_{-2}+z_0)^2}$	$\frac{C_3}{(\xi_3+z_0)^2}+\frac{C_{-3}}{(\xi_{-3}+z_0)^2}$	A_0', Å
10					
...					
17.86	-24.789	2.421	0.022	-0.103	-22.448
18	-20.680	2.794	-0.017	-0.094	-17.997
19	-16.349	3.262	-0.072	+0.081	-13.239
20	-14.338	3.509	-0.105	+0.073	-11.007
21	-13.303	3.644	+0.124	-0.068	- 9.851
22	-12.418	3.762	-0.143	-0.063	- 8.862
23	-11.780	3.848	-0.157	-0.060	- 8.148
24	-11.260	3.920	-0.169	-0.057	- 7.566
25	-10.863	3.975	-0.179	-0.054	- 7.122
26	-10.490	4.026	-0.189	-0.052	- 6.705
28	- 9.951	4.096	-0.204	-0.048	- 6.106
30	- 9.510	4.161	-0.216	-0.044	- 5.610
32	- 9.190	4.204	-0.226	-0.042	- 5.254
34	- 8.908	4.241	-0.235	-0.039	- 4.942

In Table 6 we give detailed calculations for the numerical evaluation of the real part of the integral

$$(7.11) \qquad \int_0^\infty r^2 \alpha(r)\, e^{irz_1}\, dr = \sum_{k=-3}^{3} \frac{C_k}{(\xi_k + z_1)^2}$$

Table 6

λ/ϵ, Å^3	$R\frac{C_0}{(\xi_0+z_1)^2}$	$R\frac{C_1}{(\xi_1+z_1)^2}$	$R\frac{C_{-1}}{(\xi_{-1}+z_1)^2}$	$R\frac{C_2}{(\xi_2+z_1)^2}$	$R\frac{C_{-2}}{(\xi_{-2}+z_1)^2}$
10	0.317	0.394	1.990	-0.048	-1.323
12	0.365	0.384	2.166	-0.045	-1.322
15	0.419	0.371	2.349	-0.041	-1.320
16	0.433	0.368	2.398	-0.040	-1.319
17	0.447	0.365	2.441	-0.040	-1.319
17.85	0.457	0.362	2.478	-0.039	-1.318
17.86	0.457	0.362	2.478	-0.039	-1.318
18	0.459	0.362	2.480	-0.039	-1.318
19	0.470	0.359	2.517	-0.038	-1.317
20	0.480	0.357	2.548	-0.038	-1.317
21	0.489	0.355	2.582	-0.037	-1.316
22	0.498	0.353	2.606	-0.037	-1.316
23	0.506	0.351	2.631	-0.036	-1.316
24	0.513	0.349	2.655	-0.036	-1.315
25	0.521	0.348	2.676	-0.035	-1.315
26	0.527	0.346	2.694	-0.035	-1.315
28	0.539	0.344	2.732	-0.034	-1.314
30	0.549	0.341	2.763	-0.034	-1.313
32	0.558	0.340	2.790	-0.033	-1.313
34	0.566	0.337	2.815	-0.033	-1.312

λ/ϵ, Å^3	$R\frac{C_3}{(\xi_3+z_1)^2}$	$R\frac{C_{-3}}{(\xi_{-3}+z_1)^2}$	B_1', Å^3
10	-0.007	0.133	1.457
12	-0.008	0.140	1.679
15	-0.009	0.117	1.886
16	-0.010	0.116	1.945
17	-0.010	0.114	1.997
17.85	-0.010	0.112	2.042
17.86	-0.010	0.112	2.042
18	-0.010	0.112	2.046
19	-0.011	0.111	2.091
20	-0.011	0.109	2.128
21	-0.011	0.108	2.170
22	-0.011	0.107	2.200
23	-0.012	0.106	2.231
24	-0.012	0.105	2.260
25	-0.012	0.104	2.287
26	-0.012	0.103	2.309
28	-0.012	0.102	2.355
30	-0.012	0.100	2.394
32	-0.013	0.099	2.429
34	-0.013	0.098	2.459

In Table 7 we give detailed calculations for the numerical evaluation of the imaginary part of the integral (7.11)

Table 7

λ/ϵ, Å^3	$J\frac{C_0}{(\xi_0+z_1)^2}$	$J\frac{C_1}{(\xi_1+z_1)^2}$	$J\frac{C_{-1}}{(\xi_{-1}+z_1)^2}$	$J\frac{C_2}{(\xi_2+z_1)^2}$	$J\frac{C_{-2}}{(\xi_{-2}+z_1)^2}$
10	-1.668	0.844	5.979	-0.257	0.761
12	-1.706	0.860	6.300	-0.259	0.815
15	-1.742	0.877	6.656	-0.262	0.874
16	-1.751	0.881	6.754	-0.262	0.889
17	-1.759	0.885	6.844	-0.263	0.902
17.85	-1.765	0.888	6.916	-0.263	0.913
17.86	-1.765	0.888	6.916	-0.263	0.913
18	-1.766	0.889	6.926	-0.263	0.915
19	-1.772	0.892	7.003	-0.264	0.926
20	-1.777	0.894	7.072	-0.264	0.936
21	-1.783	0.897	7.139	-0.264	0.946
22	-1.786	0.899	7.196	-0.264	0.954
23	-1.790	0.900	7.253	-0.265	0.962
24	-1.794	0.902	7.304	-0.265	0.969
25	-1.797	0.904	7.353	-0.265	0.976
26	-1.800	0.906	7.398	-0.265	0.982
28	-1.805	0.908	7.481	-0.266	0.993
30	-1.810	0.911	7.556	-0.266	1.003
32	-1.813	0.913	7.619	-0.266	1.011
34	-1.817	0.915	7.679	-0.266	1.019

λ/ϵ, Å^3	$J\frac{C_3}{(\xi_3+z_1)^2}$	$J\frac{C_{-3}}{(\xi_{-3}+z_1)^2}$	C_1', Å^3
10	-0.395	0.115	5.378
12	-0.399	0.116	5.727
15	-0.404	0.116	6.115
16	-0.405	0.116	6.221
17	-0.406	0.116	6.319
17.85	-0.407	0.116	6.398
17.86	-0.407	0.116	6.398
18	-0.407	0.116	6.410
19	-0.408	0.116	6.493
20	-0.409	0.116	6.568
21	-0.410	0.116	6.641
22	-0.410	0.116	6.704
23	-0.411	0.116	6.765
24	-0.412	0.116	6.821
25	-0.412	0.112	6.874
26	-0.413	0.116	6.924
28	-0.413	0.116	7.014
30	-0.414	0.116	7.096
32	-0.415	0.116	7.166
34	-0.416	0.116	7.230

Similar calculations have been made for

$$(7.12) \qquad \frac{\beta'(z_u)}{z_u} = -\frac{4}{(2\pi)^{1/2}} \sum_{k=-3}^{3} \frac{C_k}{(\xi_k^2 - z_u^2)^2}$$

For which in Table 8 we give the final result.

Table 8

λ/ϵ, Å^3	A_0'', Å^5	A_1'', Å^5	B_1'', Å^5
10		22.01	83.98
12		33.12	117.0
15		53.79	176.8
16		62.04	199.5
17		70.55	223.9
17.85		78.61	245.6
17.86	-444.9	78.61	245.6
18	-453.2	79.75	249.4
19	-496.4	89.90	276.4
20	-547.2	99.10	304.5
21	-590.8	111.57	334.8
22	-644.3	122.1	365.1
23	-697.8	134.2	398.1
24	-754.6	146.6	432.2
25	-808.7	159.2	463.7
26	-873.4	172.7	503.3
28	-996.7	202.7	581.2
30	-1138.8	232.3	662.5
32	-1280.9	266.8	757.0
34	-1440.5	300.8	846.8

4. The calculation of ϵ and the equation of state for T=150°K.

In chapter III we obtained an explicit expression for the parameter ϵ ,namely

$$\epsilon = \frac{\mathcal{A}}{\mathcal{A}+\mathcal{B}+C} \tag{7.13}$$

where

$$\mathcal{A} = \int_0^\infty r^2 \alpha(r)\, dr = -\sum_k \frac{C_k}{\xi_k^2} = 22.38\,\text{Å}^3 \tag{7.14}$$

$$\mathcal{B} = \int_0^\infty r^2 \alpha(r)^2\, dr = -\sum_{k,s} \frac{C_k C_s}{i(\xi_k+\xi_s)} = 30.79\,\text{Å}^3 \tag{7.15}$$

and

$$C = (2\pi)^{1/2}\left(\frac{\lambda}{\epsilon}\right)^2 \sum \frac{z_u}{\beta'(z_u)} \int_0^\infty r\alpha(r)\, e^{irz_u}\, dr\,. \tag{7.16}$$

In Table 9 we give the values of C as well as the final result for ϵ as function of density.

Finally,using our equation of state (6.1) and the results obtained in the last three sections we have calculated the isotherm for T=150° K. In Table 10, the pressure p is given as function of volume,for a c.c of gas at normal pressure and temperature. The pressure p is expressed in atmospheres and the volume V in c.c.

Table 9

χ_6, Å^3	C, Å^3	ϵ	λ, Å^3
10	-13.47	0.56	5.63
12	-14.56	0.58	6.95
15	-15.77	0.60	8.97
16	-16.08	0.60	9.65
17	-16.36	0.61	10.33
17.85	-16.58	0.61	10.91
17.86	-18.82	0.65	11.62
18	-17.84	0.63	11.39
19	-16.94	0.62	11.73
20	-16.63	0.61	12.24
21	-16.48	0.61	12.80
22	-16.45	0.61	13.40
23	-16.40	0.61	13.99
24	-16.40	0.61	14.60
25	-16.56	0.61	15.27
26	-16.48	0.61	15.85
28	-16.53	0.61	17.09
30	-16.67	0.61	18.39
32	-16.60	0.61	19.57
34	-16.79	0.61	20.91

Table 10

V, c.c.	p, atm.
0.00239	41.7
0.00295	53.3
0.00381	57.6
0.00410	57.6
0.00439	57.3
0.00464	56.7
0.00484	52.0
0.00494	49.6
0.00499	54.3
0.00521	54.9
0.00545	54.7
0.00570	54.2
0.00595	53.7
0.00621	52.9
0.00650	51.6
0.00674	51.1
0.00727	49.3
0.00782	47.3
0.00833	45.8
0.00890	43.9

In figure 8 we have plotted our results for T=150° K.

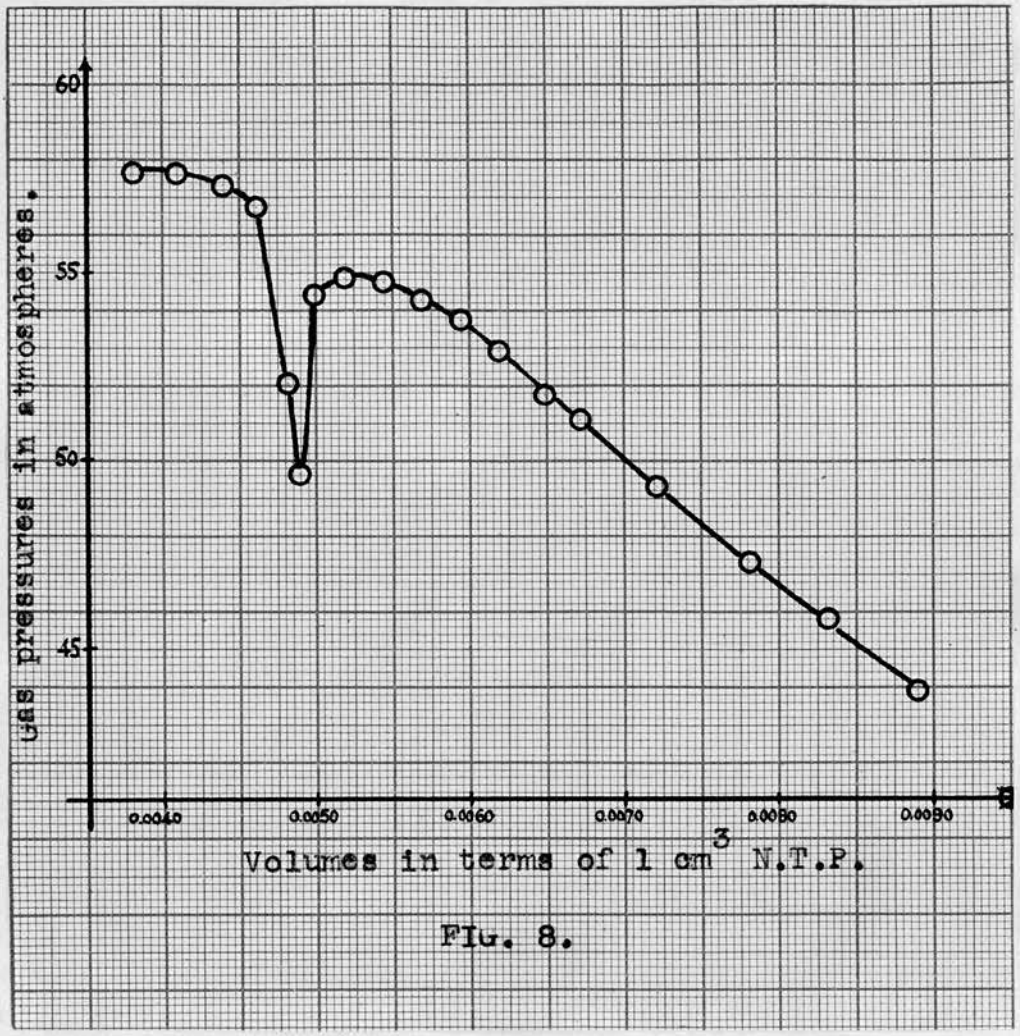


FIG. 8.

The isotherm just obtained does not correspond exactly with that of the critical temperature, but to a lower one. If one assumes that the maximum of the curve in the gas region gives approximately the critical volume V_c, one obtains for it the value

$$V_c = 0.0052 \text{ c.c.}$$

The experimental value $V_c^{(e)}$, which we have taken from 'International Critical Tables', gives

$$V_c^{(e)} = 0.0034 \text{ c.c.}$$

The calculated critical pressure, according to the same assumption, is

$$p_c = 54 \text{ atmospheres}$$

Experiment gives

$$p_c^{(e)} = 50 \text{ atmospheres}$$

5. <u>The equation of state for $T = 130°K$.</u>

Similar calculations to those performed for $T = 150°K$. have been made for $T = 130°K$. Figure 9 shows the final result.

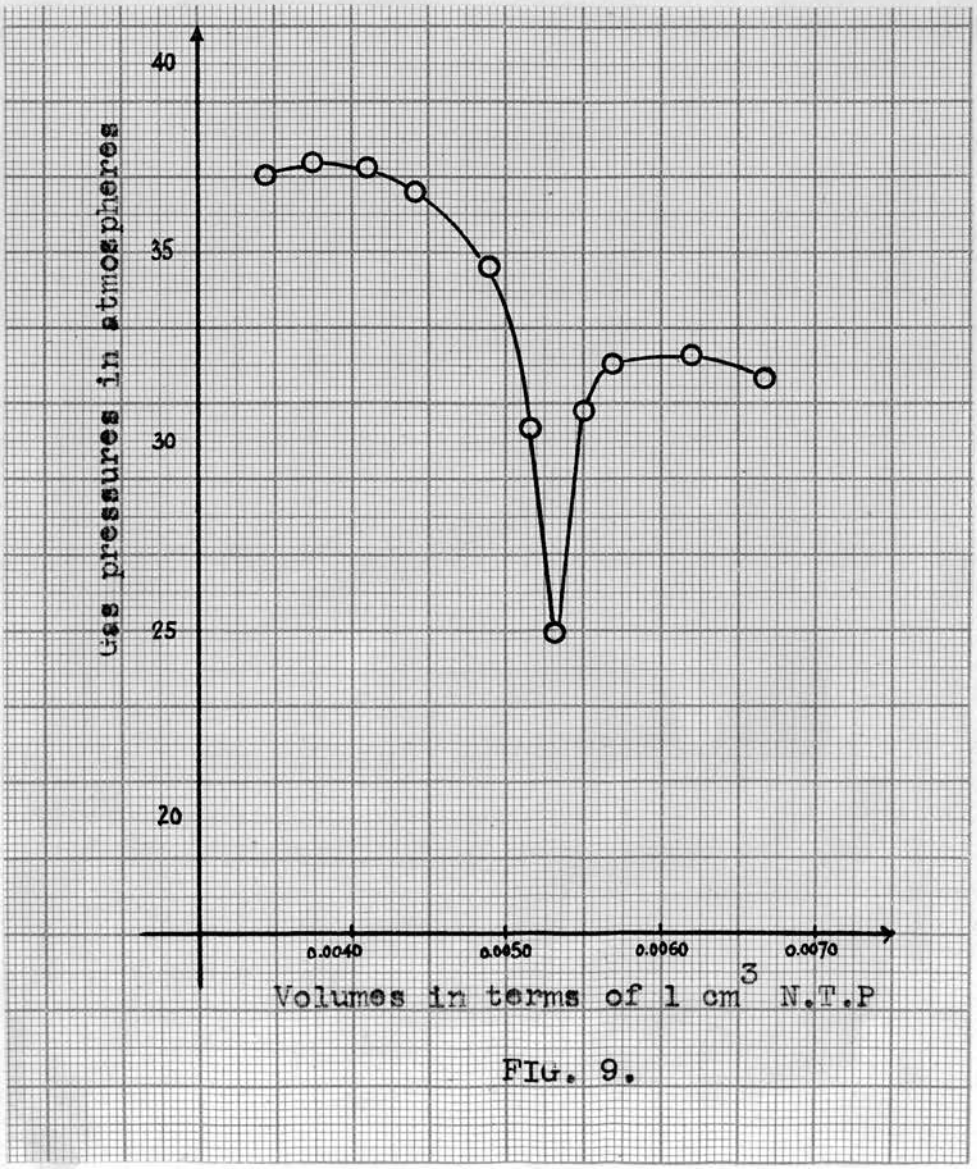


FIG. 9.

CONCLUSION.

The results obtained in this investigation confirm the views expressed in the theory of Born and Green dealing with the extension of the validity of the equation of state to the liquid region. At the present stage of development, however, an exact quantitative description of the facts eludes us. Considering the several assumptions made in obtaining the final equation of state, it would therefore appear that attention should be concentrated on improving the approximation arrived at through the introduction of the averaging parameter ϵ.

Nevertheless there does emerge a clear qualitative picture of what happens in the transition from the liquid to the gas phase; and, moreover, the method used for the actual evaluation of the expressions appearing in the equation of state, is now being used by the author, with satisfactorily results, for the solution of problems connected with the radial distribution function.

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